

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 06/00/78		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE ROCKY MOUNTAIN ARSENAL NORTH BOUNDARY WATER TREATMENT PROCESS, FINAL REPORT			5. FUNDING NUMBERS	
6. AUTHOR(S)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ROCKY MOUNTAIN ARSENAL (CO.) COMMERCE CITY, CO			8. PERFORMING ORGANIZATION REPORT NUMBER 81339R15	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) IN COMPLIANCE WITH THE CDH CEASE AND DESIST ORDERS, THIS VALUE ENGINEERING STUDY DEALS ONLY WITH THE SUBSURFACE WATER FLOW PROBLEMS AT RMA. THE MAJOR EXTENT OF THE SUBSURFACE FLOW HAS BEEN FOUND IN AN AREA ALONG THE NORTHERN BOUNDARY OF THE ARSENAL. UNTIL THE SOURCE LOCATIONS CAN BE IDENTIFIED AND CLEANED UP, THIS SUBSTANCE FLOW WILL BE BLOCKED WITH A BARRIER, DEWATERED VIA A WELL SYSTEM, CLEANED UP THROUGH A PROCESS PLANT, AND RETURNED TO THE AQUIFER ON THE OTHER SIDE OF THE BARRIER THROUGH RECHARGE WELLS. THIS STUDY SPECIFICALLY DEALS WITH THE WATER TREATMENT PROCESS TO BE UTILIZED. A GENERAL OUTLINE OF THE RMA NORTH BOUNDARY IS INCLUDED.				
<div style="text-align: center; font-size: 2em; font-weight: bold;">19950130 070</div> <div style="text-align: right; font-weight: bold;">DTIC QUALITY INSPECTED 3</div>				
14. SUBJECT TERMS POWDERED CARBON, GRANULAR CARBON, COST, DIMP, DCPD			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

VALUE ENGINEERING STUDY 77-5

81339R15
originalROCKY MOUNTAIN ARSENAL NORTH BOUNDARY
WATER TREATMENT PROCESS

AT

ROCKY MOUNTAIN ARSENAL
Commerce City, Colorado 80022Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

FINAL REPORT

June 1978

FILE COPY

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

RICHARD WELLING
Inds. Eng.
Proc. Dev. & Eval. DivFile
RMA Dec 1978

1. The Value Engineering Team for this groundwater clarification system study consisted of the following Rocky Mountain Arsenal personnel:

Richard Welling	Industrial Engineer	Chairman
Rudolph Sweder	Industrial Engineer	Member
Dennis Prusinski	Chemical Engineer	Member

The procedures used for this study follow those published in the "Principles and Applications of Value Engineering," USAMETA Course Book, Rock Island, Ill., Sept 1973. The format for this final report basically follows the outline on Page 6-4 of the cited book.

2. PROBLEM DESCRIPTION: As a result of prior industrial operations at Rocky Mountain Arsenal various contaminants have been released beyond the Arsenal boundaries through surface and subsurface water streams. Industrial type operations have been conducted at Rocky Mountain Arsenal for over 35 years. In addition, to the U.S. Army operations, Shell Chemical Company is manufacturing herbicides and insecticides at RMA under a lease agreement. In May 1974, diisopropylmethylphosphonate (DIMP) and dicyclopentadiene (DCPD) were detected in surface water draining from a marshy bog on the northern boundary of the Arsenal. In December 1974, the Colorado Department of Health detected DIMP in a well near the city of Brighton, Colorado. These discoveries led the State of Colorado Department of Health to issue three Cease and Desist Orders on 7 April 1975 against Shell Chemical Company (SCC) and Rocky Mountain Arsenal (RMA). In short, these orders stated that SCC and RMA must:

- a. Immediately stop the off-post discharge (both surface and subsurface) of DIMP and DCPD.
- b. Take action to preclude future off-post discharge (both surface and subsurface) of DIMP and DCPD.

- c. Provide written notice of compliance with Item a.
- d. Submit a proposed plan to meet the requirements of Item b.
- e. Develop and institute a surveillance plan to verify compliance with Items a and b.

This value engineering study deals only with the subsurface flow problem. The major extent of the subsurface flow has been found in an area along the northern boundary of the Arsenal. Until the source locations can be identified and cleaned up this subsurface flow will be blocked with a barrier, dewatered via a well system, cleaned up through a process plant, and returned to the aquifer on the other side of the barrier through recharge wells. This study specifically deals with the water treatment process to be utilized. A general outline of the RMA North Boundary is included in Attachment 1.

3. Present Method: The method originally selected for water treatment was carbon adsorption utilizing powdered carbon in an upflow clarifier. This process selection was arrived at through a logical and sequential developmental path. In summary, the processing problem was recognized as being treatment of subsurface waters at the north boundary of RMA. Immediately adjacent to the area where water would be pumped from there is a bog. This bog is created from subsurface waters being discharged to the surface through a fault. This water was selected for use in evaluating candidate treatment processes. Using the expertise and prior experience of MERADCOM, an evaluation of treatment methodologies for the selected water was performed. Carbon adsorption was selected and isotherms were run using various carbons (granular and powdered). Powdered carbon produced the optimum results. Fortunately, MERADCOM had both 420 gph and 10,000 gph treatment plants available for use in experimental verification

of treatment capabilities.. Extensive experimental runs were performed using bog water and the 420 gph unit. To form and maintain a carbon bed it was necessary to use both cationic and anionic resin flocculants. The key operating parameters (flow rate, carbon dosage, anionic and cationic quantities, etc.) were varied and the system operating parameters optimized. At this time it was realized that virtually any reasonable removal rate for DIMP and DCPD could be achieved with this process. To verify the scale up factors the 10,000 gph unit was operated on bog water for a short period. This test confirmed the feasibility of full-scale operations. Water was then obtained from wells at the site of the proposed barrier. This water was then processed through the 420 gph unit and the potential removal efficiency was verified. The well waters were notably different from the bog water. While DIMP was at the 400-450 ppb level in the bog, it was close to 1500 ppb in the well waters. It was at this stage of development (prior to final commitment to proceed with a powdered carbon water treatment facility) that this value engineering study was accomplished. While powdered carbon will achieve the removal efficiencies desired it was recognized that sludge handling problems remained to be solved and that the actual subsurface water to be treated was of a different character than the bog water on which this process development was based. A general powdered carbon process flow diagram is provided in Attachment 2.

4. Proposed Alternative: Several alternatives were considered prior to system selection. These included reverse-osmosis, UV-O₃, resins, powdered carbon, and granular carbon. Carbon adsorption remained the best alternative due to the high removal efficiency for the organic contaminants involved and the low energy requirements for system operation. A rerun of carbon adsorption isotherms using well water (more representative of actual

conditions than bog water) showed granular carbon to be more efficient than the powdered carbon. Studies using both virgin and reactivated carbon were performed by Calgon Corporation under contract. The removal efficiencies were an improvement over powdered carbon. More significantly, the granular carbon could be reactivated and reused; hence, no sludge handling problem. Using Calgon Corporation's reactivation facilities it was verified that reactivation could easily be accomplished while meeting EPA air quality standards. The comparison of virgin and reactivated carbons showed reactivated carbon to be slightly more efficient at DIMP removal. These studies showed granular carbon to be more desirable than powdered carbon for the boundary treatment system. Following this conclusion studies on how best to utilize granular carbon were performed. Considering the availability of a 10,000 gph erdlator, studies using granular carbon were performed using the similar 420 gph unit. Numerous problems were encountered (unit required modification to prevent "clumping" of carbon in the downcomer feed system and the maintenance of a bed at required flow rates was extremely difficult to establish and maintain). It was concluded that usage of granular carbon in this system would be unreliable and require constant attention. The simplest and most reliable method for using granular carbon is to utilize confined columns and/or tanks. When the carbon is saturated the entire carbon stock would be exchanged with the old carbon reactivated for reuse. This system requires very few manhours since only infrequent monitoring and sampling is required. Two options remained to be evaluated; (1) complete purchase of all processing and reactivation equipment by RMA or, (2) obtaining an equipment lease and service contract that includes carbon reactivation. Considering the large capital investment and operating personnel

requirements for a carbon reactivation facility the decision in favor of a service contract becomes obvious. Since the operating life for the north boundary treatment system is extremely difficult to forecast, a decision in favor of leased equipment is most reasonable. In addition, obtaining a turnkey system provides a proven and tested system and relieves RMA of the high engineering, development, testing and modification costs. Since Calgon Corporation is the only vendor offering a turnkey service contract for water treatment using granular carbon (including carbon reactivation) the decision to obtain a Calgon Corp. service contract was made. A general process flow diagram is included as Attachment 3. Attachments 4 and 5 provide some general reference data on DIMP and DCPD.

5. Conclusions: The removal of DIMP and DCPD from subsurface flows off Rocky Mountain Arsenal to comply with the State of Colorado Cease and Desist Order can most economically and reliably be achieved through a service contract with Calgon Corporation. This granular carbon system eliminates the expensive sludge handling problems encountered with powdered carbon and allows reactivation and reuse of spent carbon (included in the service contract). The granular carbon system is not energy intensive and requires less operator manhours than other systems considered (system requires monitoring rather than constant operator attention). Considerable operational cost savings are accrued as a result of less operator manhours and elimination of sludge processing. The system is easily expanded to permit handling larger flow rates if required or to add additional processes if treatment of additional contaminants becomes necessary (fluorides, etc.). Leasing of all processing equipment eliminates the expensive design, development and testing cycle in addition to large capital investment costs. The system life is indefinite;

therefore, leasing is again favored. In summary, analysis of system efficiency, effectiveness, reliability, operating costs, initial capital investment requirements and future expansion capabilities, all favor the service contract with Calgon Corporation.

6. Cost Summary: All costs for the powdered carbon process and sludge disposal are based on studies conducted by the Department of the Army. All costs for the granular carbon process are based on firm quotes from Calgon Corporation. Annual operating costs for both units (see Table 6-1) are based on processing 10,000 gallons of water per hour, 24 hours per day, 330 days per year even though field tests indicate that the powdered carbon process cannot maintain a stable bed at 10,000 gph. Material costs for the powdered carbon process are based on the optimum carbon and coagulant feed rates established during the well water studies. A maximum operating period of six years is assumed so only routine maintenance is listed for the powdered carbon equipment. The annual service contract for the granular carbon process includes maintenance and reactivation of three carbon beds. The \$8,000.00 listed for material is a contingency fund in the event a fourth carbon bed must be reactivated. The \$10,000.00 for the granular carbon process is for utilities installation and operation. Attachment 6 provides a summary of the powdered carbon system cost analysis.

ITEM	POWDERED CARBON PROCESS	GRANULAR CARBON PROCESS
Service Contract ¹	-0-	125,000.00
Material	41,621.00✓	8,000.00✓
Labor	266,240.00✓	40,000.00✓
Maintenance, Utilities, etc.	34,400.00	10,000.00
TOTAL	342,261.00 ²	183,000.00

1. The powdered carbon process requires an initial capital investment of \$84,000.00;
The granular carbon process requires an initial capital investment of \$140,000.00
2. Does not include sludge disposal costs

Table 6-1. Annual Operating Costs Less Inflation

Operation of the powdered carbon process requires some method of sludge disposal. Since there are four options, the annual costs have not been listed in Table 6-1. Figures 6-1 and 6-2 graphically depict the total costs for the three and six year programs respectively. These bar graphs present all four sludge disposal options and include an annual inflation rate of 6.5 percent. Figure 6-3 also includes the inflation rate and shows the cost per 1000 gallons treated for both the three and six year programs. Except for the powdered carbon process, amortization of the original capital costs over six years instead of three years reduces the cost per 1000 gallons for six years. Since labor is the primary expense for the powdered carbon operation, labor inflation costs exceed equipment amortization gains and increases the cost per 1000 gallons over six years. Any cost comparison between the two processes show the granular carbon process to be economically advantageous. Evaluation of both processes with respect to the full scale process guidelines dictates that the Calgon Corporation granular carbon process unit be selected for the Interim Containment/Treatment System. Considering the difference in initial capital investments (without considering sludge disposal costs) the first year savings are \$103,261.00. The following years have a net saving of \$159,261.00 each year. Assuming a conservative six years of system operation the Calgon service contract will save \$899,566.00 over the usage of powdered carbon without considering sludge disposal costs. Using the least cost method of sludge disposal that is acceptable (landfill) the powdered carbon process will require an additional \$900,000.00 in operating costs. Hence, the total savings for the Calgon Corporation service contract will be \$1,799,566.00 over the forecast six year operating period.

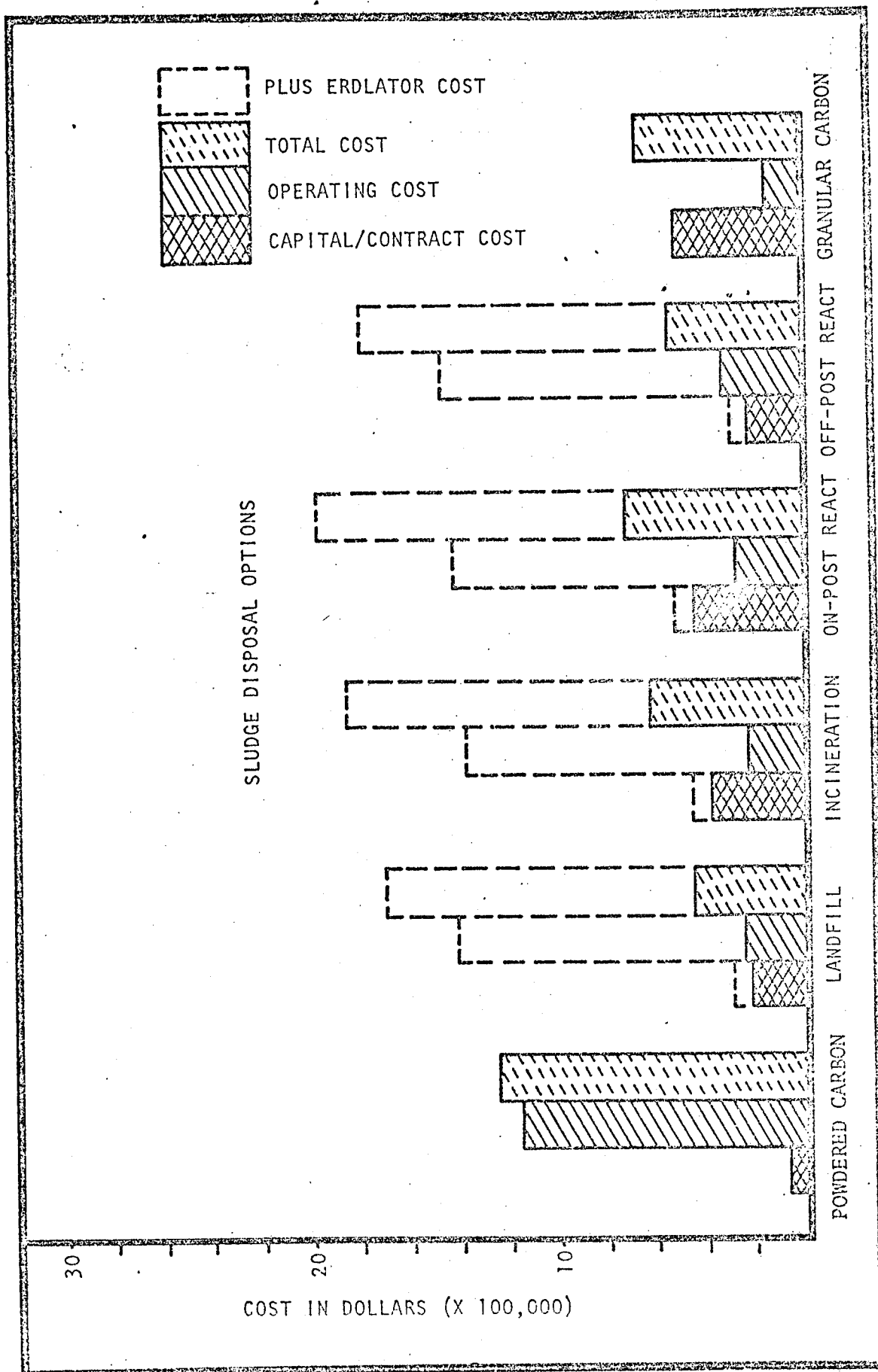


Figure 6-1. Total Costs for Three Year Program

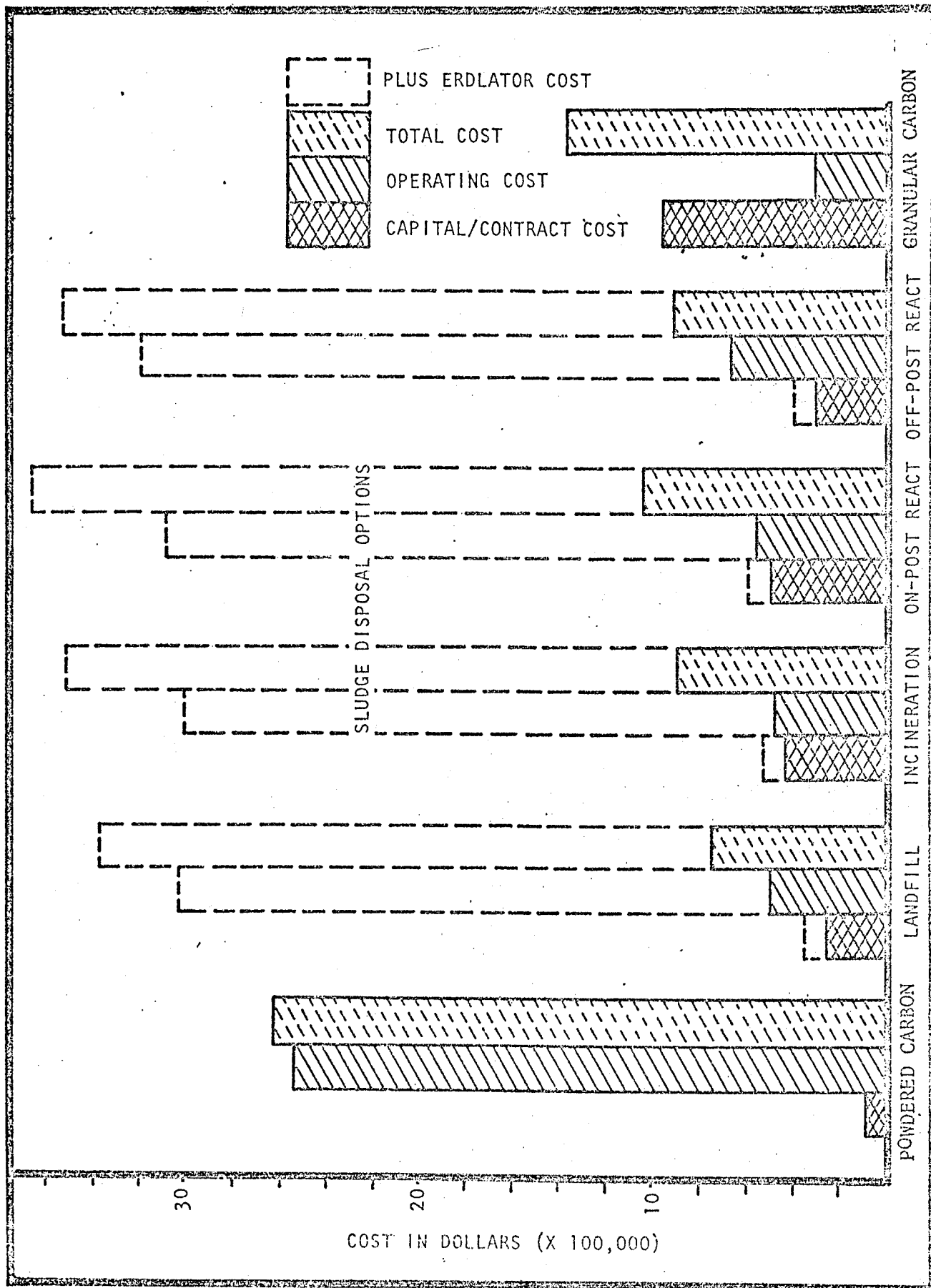


Figure 6-2. Total Costs for Six Year Program

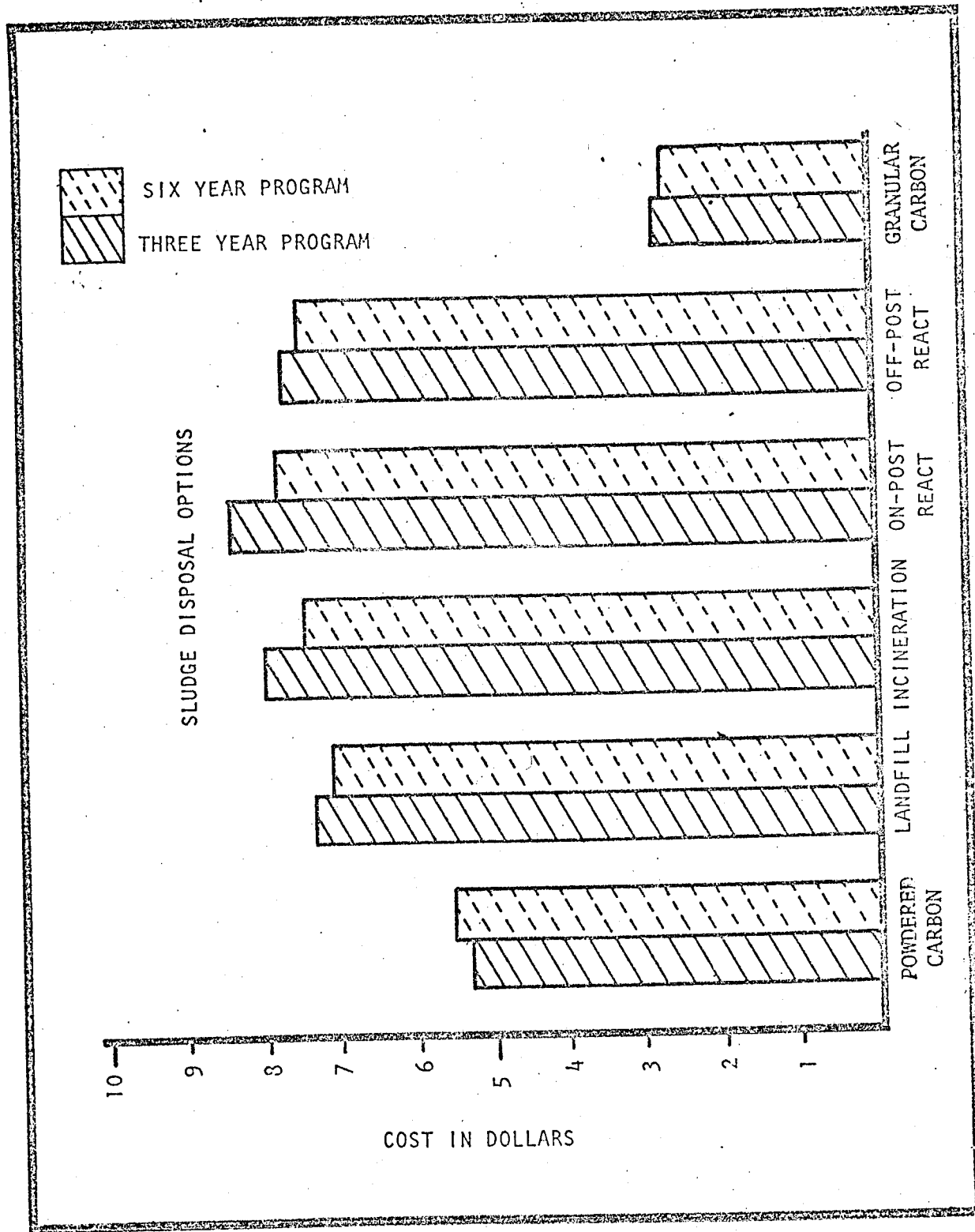
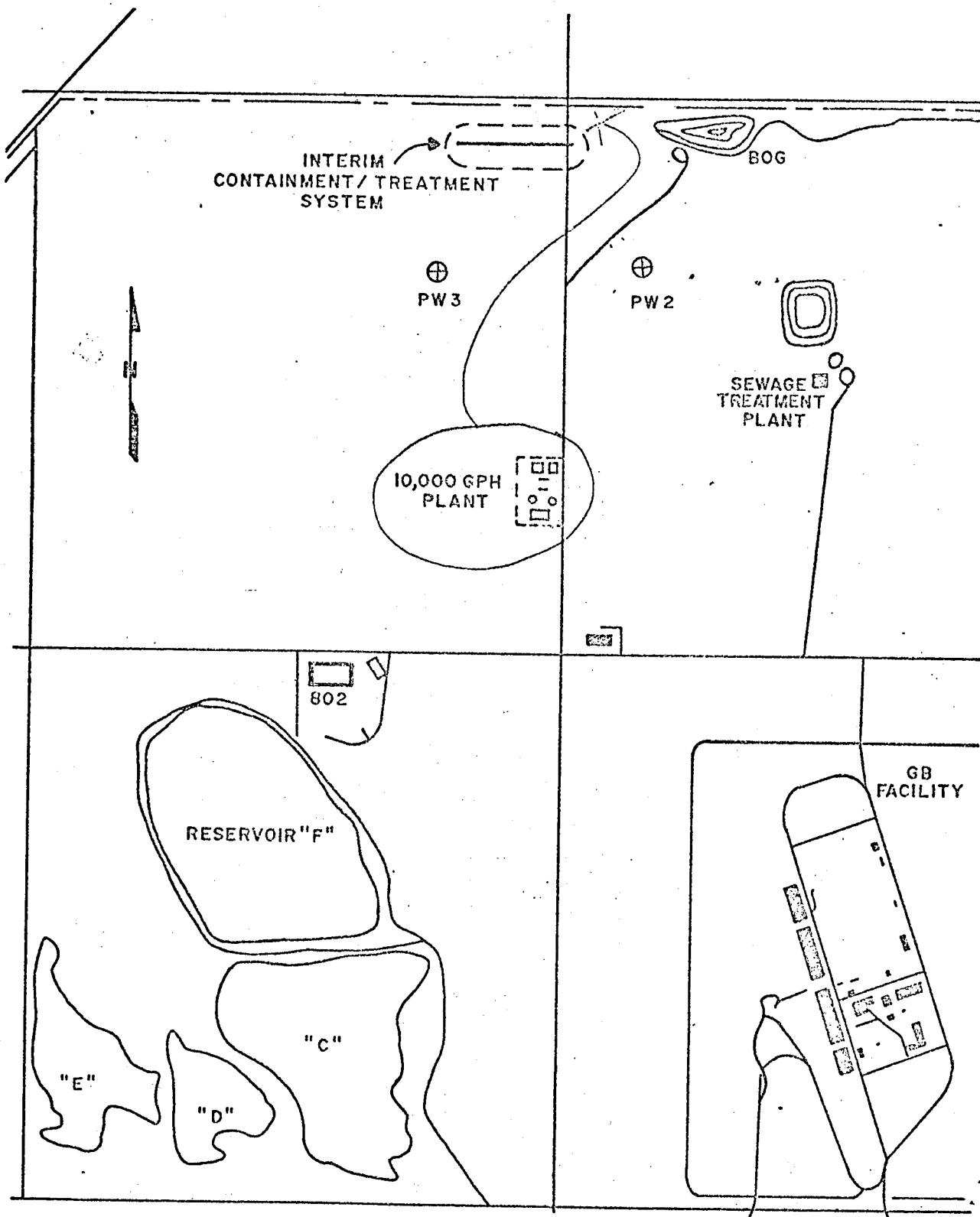
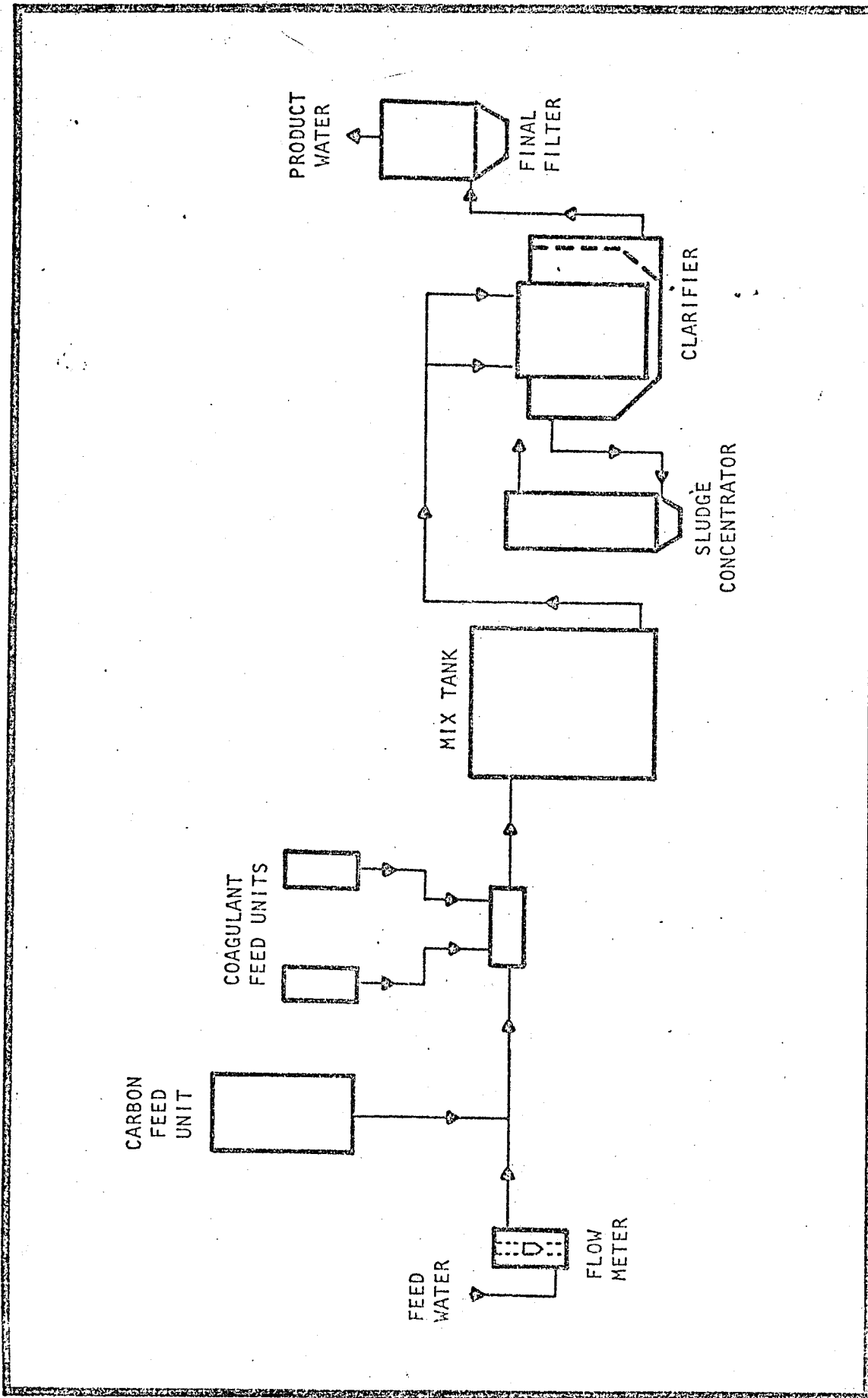


Figure 6-3. Costs per 1000 Gallons for Three and Six Year Programs

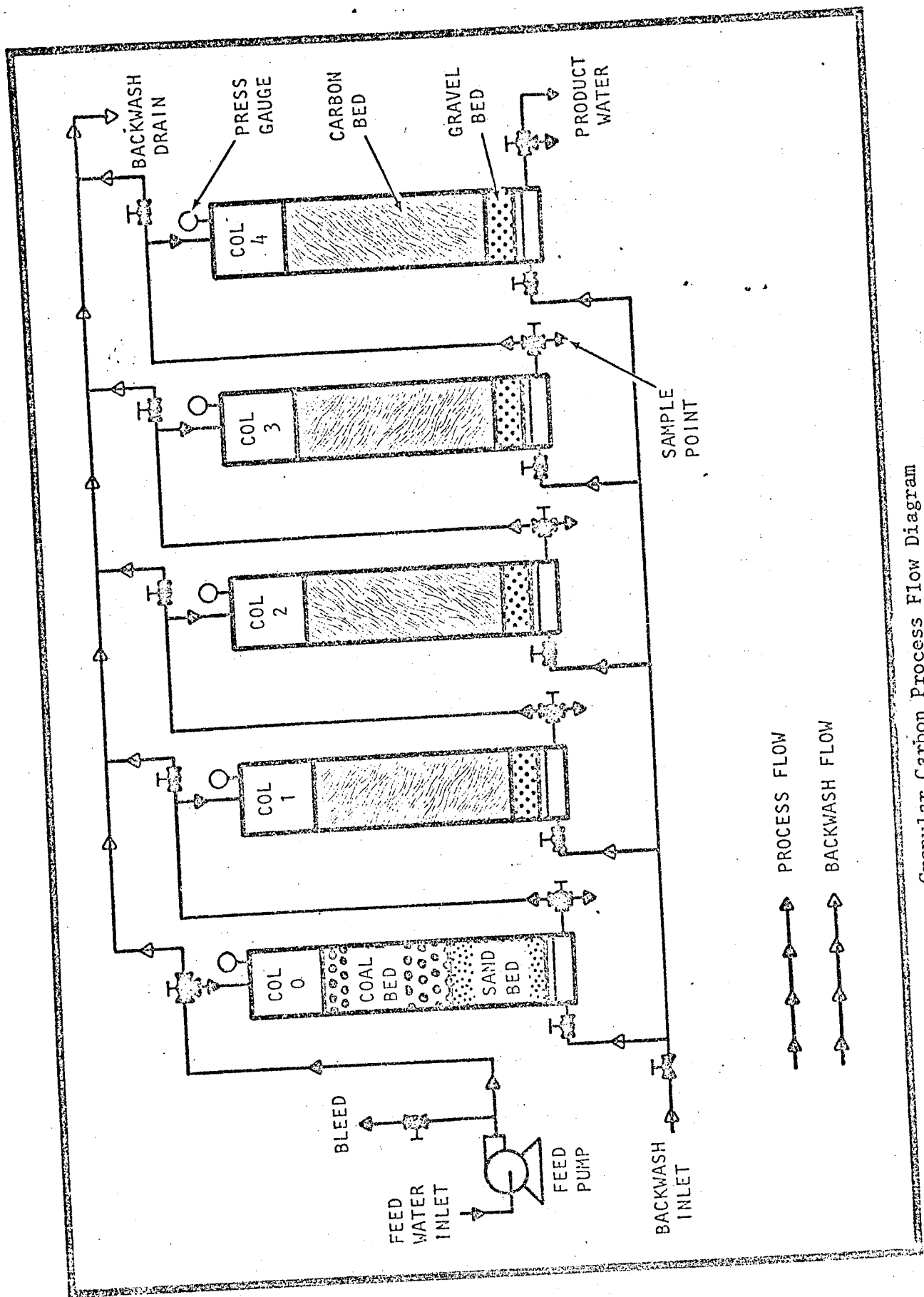
7. Implementation: Bench scale process studies, full-scale engineering design, signing of a contract for the north boundary treatment service and construction start-up have been accomplished. Final treatment plant construction and system testing will be completed in June 1978. System full time operation will begin when the barrier system construction is completed (estimated at Aug 1978). During the barrier construction phase the treatment plant will occasionally be needed to maintain the subsurface flows.



RMA North Boundary Plan View



Powdered Carbon Process Flow Diagram



Granular Carbon Process Flow Diagram

DIISOPROPYL METHYLPHOSPHONATE

ALTERNATIVE NAMES

Diisopropyl methylphosphonate; DIMP; phosphonic acid, methyl-, bis-(1-methylethyl) ester (Chem. Abstr. after 1971); phosphonic acid, methyl-, diisopropyl ester (1947-1971); methanephosphonic acid, diisopropyl ester.

PHYSICAL AND CHEMICAL PROPERTIES

CAS Reg. No. 1445-75-6

Toxic Substances List: Not listed

Edgewood Arsenal Number: EA 1250

Wiswesser Line Notation: TY&OP0&1&0Y

Molecular formula: $C_7H_{17}O_3P$

Structural formula: $((CH_3)_2CHO)_2(CH_3)P=O$

DIMP is a liquid at room temperature with $n_D^{20} = 1.4112$ (1), a bulk density at 25°C of 0.976 g/cc and a boiling point of 174°C (2,3). Its vapor pressure-temperature behavior is closely approximated by the following empirical relationship (2, 3).

$$\log P \text{ (mm of Hg)} = 9.8571 - 3105/T(^{\circ}K)$$

DIMP is best synthesized through the reaction of methyl iodide with triisopropyl phosphite (4, 5). Other methods are mentioned in the patent literature (6, 7, 8).

Very little is known of DIMP solubility in water. In studies of DIMP hydrolysis in acidic and basic solutions (9), 0.12 N or higher DIMP was used at temperatures above 80°C, indicating solubilities of above 11 g/liter in that temperature range. In DIMP studies at Southeast Research Institute (10), the solubility in water at 25°C was between 1 and 2 g/liter.

DIMP hydrolysis rates in water at 98, 90 and 80°C have been reported as 2×10^{-6} , 0.88×10^{-6} and $0.31 \times 10^{-6} \text{ sec}^{-1}$ respectively (11). The hydrolysis activation energy was estimated to be 26.9 Kcal/mole. These reaction rates can be used to predict hydrolytic behavior at 10°C, a temperature more representative of ground water in a temperate climate. The estimated rate is $3.2 \times 10^{-11} \text{ sec}^{-1}$, corresponding to a hydrolysis half-life of about 687 years. In studies cited previously (9), DIMP was among a series of alkylphosphonate esters whose hydrolysis characteristics were measured. In 1N HCl solution, rate constants of 1.74×10^{-4} , 2.81×10^{-4} , 4.78×10^{-4} , 8.53×10^{-4} and $8.56 \times 10^{-4} \text{ sec}^{-1}$ were determined at 88.9, 94.4, 99.7, 104.8 and 105.9 C, respectively (9). The acid hydrolysis appears to proceed by the S_N1 mechanism, since the rate of DIMP hydrolysis is greater than that of the lower alkyl phosphonate esters. Basic hydrolysis appears to proceed by the S_N2 mechanism, since the DIMP hydrolysis

rate is less than that of the lower alkylphosphonate esters. Typical rate constants for 0.12 N DIMP in 0.2N NaOH solution were 1.53×10^{-4} , 2.29×10^{-4} , and 4.82×10^{-4} M sec⁻¹ at 80, 90 and 100°C respectively. Basic hydrolysis at elevated temperatures is a convenient way to prepare the monoester, isopropyl methylphosphonate. In DIMP studies at Southeast Research Institute (10), the mono-sodium salt of DIMP was prepared by dissolving DIMP in 2N NaOH, heating to 50°C, followed by slow cooling to room temperature, with stirring applied throughout the process. About four days were required for completion of the hydrolysis reaction. It would appear that at room temperature and mildly basic conditions, hydrolysis of DIMP would be quite slow. DIMP is formed from sodium isopropyl methylphosphonate at 270°, but DIMP is also converted, in part, to trimethylphosphine oxide at this temperature (12). DIMP is decomposed almost entirely on short residence in a microwave plasma discharge (13); among the products are methylphosphonic acid, isopropyl methylphosphonate, phosphoric acid, isopropyl alcohol, and propylene.

DIMP forms a number of metal complexes in the absence of moisture (14, 15, 16).

DIMP does not appear to be a cholinesterase inhibitor (17).

ANALYTICAL METHODS

DIMP analysis by infrared and Raman spectra was reported by Meyrick and Thompson in 1950 (18). Strong infrared bands occur at 504, 983, 1008, 1248 (phosphonyl), and 2983 cm⁻¹, while strong Raman bands occur at 710, 1445, 2930 and 2985 cm⁻¹. Christol, Levy and Marty listed infrared absorptions at 987, 1015 and 1244 (phosphonyl) cm⁻¹. Moores (19) reported absorptions at 899, 1239 and 1314 cm⁻¹. The spectrum of DIMP was also studied by Lorquet and Vassart (20). Unfortunately, other alkylphosphonate esters have similar absorption bands.

Thin-layer and paper chromatography methods for DIMP have been studied (21). A 2:1:1 v/v solution of hexane-benzene-methanol or a 6:1:1 v/v solution of hexane-methanol-diethyl ether was used to develop the paper chromatogram. Spots were made visible with a spray of 1% cobalt chloride in anhydrous acetone, which detected DIMP and other phosphorous esters. These esters appeared at room temperature as blue spots, which could be distinguished by their relative R_f values. DIMP detection levels were not given.

Gas chromatography has been used to analyze DIMP in water with a flame ionization detector. Two methods are known; one developed by Shell Chemical Company (22) and adopted by the Colorado Department of Health (23) and one developed at Edgewood Arsenal (12). The Colorado Department of Health methodology (23) involves extraction of DIMP from water with chloroform. Three ml of chloroform suffices to extract 85-90% of DIMP from 200 ml of water. The glass chromatographic column was 5 ft long, ¼ inch in diameter, and filled with OV-17/Reoplex on 400 CRG. A 1 ppm solution of DIMP in chloroform was used as a standard.

The Edgewood Arsenal work (12) was oriented towards determining components of waste from demilitarized methyl isopropylphosphonofluoridate (GB). The waste is extracted with methylene chloride. The chromatography column was of glass, 6 ft long x 1/4 inch in diameter and filled with QF-1 in 60-80 mesh Gas Chrom Q. GB could be detected by phosphorus flame photometry as 20 ppb (12); no limits were mentioned for DIMP or other compounds. Field ionization mass spectrometry (24) can be used to detect as little as 0.2 ppb (mole ratio), i.e., 10^{-9} g/liter.

The nuclear magnetic resonance spectrum of DIMP at 25 MHz was studied by Mavel and Martin (25).

MAMMALIAN TOXICOLOGY

No published information is available on the toxicity of DIMP to humans or experimental animals. Unpublished acute toxicity data (LD50) on experimental animals were obtained from the files at Edgewood Arsenal, and are summarized in Table E-1.

TABLE E-1
Summary of Acute Toxicity of DIMP

Animal Species	Route of Administration	LD50 (mg/kg)	Remarks	References
Mouse	Intraperitoneal	>250		26
Rat	Subcutaneous	>200		27
Rabbit	Subcutaneous	>100 <200		27
Rabbit	Intravenous	224	Local irritation 179-280 (19/20 confidence limits)	28
Rabbit	Dermal	>200	No irritation at application site	28

The toxicology of DIMP, including acute data, phytotoxicity and detoxification studies have been summarized in a fact sheet (2). No evidence was found that DIMP has been studied for carcinogenic, mutagenic or teratogenic activity in vitro. One report (17) stated that DIMP does not inhibit the enzyme cholinesterase, although no experimental evidence was given for the statement.

It is concluded from the data presented above, that DIMP is fairly toxic to experimental animals and could be irritating or corrosive to the eyes. The lack of complete data indicates the need for further studies to accurately evaluate the potential toxicity of DIMP. Recommendations for further toxicological studies were made (2) and these have been implemented through a USAMRDC contract with

Litton Bionetics, Inc., Falls Church, Virginia 22046.

An additional study on DIMP has been initiated (May 1975) in the Toxicology Division, Biomedical Laboratory, Edgewood Arsenal, APG, MD (29). This work includes a 26 week subacute study and a reproduction study in rats only.

ENVIRONMENTAL CONSIDERATIONS

No information was found as to DIMP behavior in soil and water, its effect on animals in the environment, or its transmittal in food chains. A USAMRDC contract study to determine the toxicity of DIMP to aquatic vertebrates and invertebrates has been initiated through Bionomics, E. G. & G., Inc., Wareham, MA 02571.

PLANTS

Evaluation of DIMP at Ft. Detrick during 1974-1975 indicated that DIMP could injure wheat and beans (Witchita wheat and Black Valentine beans) (30). In one test, treatment of wheat and beans (water solution to soil) with 10 ppm DIMP produced no effect on wheat, but gave a burning on edges of bean leaves. In a second test, treatment with 10 ppm or 40 ppm levels of DIMP resulted in tip burn of leaves on both wheat and beans at both levels. In other tests where DIMP and dicyclopentadiene (DCPD) were used together, there was an indication of additive or synergistic effects due to DCPD. DIMP may also be phytotoxic to sugar beets (31). In herbicidal screening tests at Ft. Detrick, rice, morning glory, bean, oat and soybean plants growing in pots in a greenhouse and sprayed with DIMP at 0.1 and 1.0 pounds per acre exhibited no injurious effects from the DIMP (32). A USAMRDC contract study to determine plant uptake and effects and soil retention of DIMP has been initiated through Aerojet Ordnance and Manufacturing Co., Downey, CA 90241.

EXISTING STANDARDS

No information available.

LITERATURE CITED

1. Gryszkiewicz-Trochimowski, E., M. Bousquet and J. Quinchon, "Preparation and Properties of Dialkyl Methylphosphonates and Dialkyl Methylthiophosphonates," *Bull. Soc. Chim. France*, 1222-1225 (1961); *C.A.*, 56, 129331 (1962).
2. Dacre, J. C., USAMBRDL, "Fact Sheet-DIMP Toxicity," (may, 1975).
3. Jonas, L., Edgewood Arsenal, MD., "Physical Properties of DIMP," personal communication (telephone), (April 7, 1975).
4. Ford-Moore, A. H. and B. J. Perry, "Diisopropyl Methylphosphonate," *Org. Syntheses*, 31, 33-35 (1951).
5. Ford-Moore, A. H. and J. H. Williams, "The Reaction Between Trialkyl Phosphites and Alkyl Halides," *J. Chem. Soc.*, 1465-1467 (1947).
6. Kearney, J. A. and C. J. Smith, Jr., "Dialkyl Alkylphosphonates, U.S. 3,179,690, (April 20, 1965); *C.A.*, 63, 632g (1965).
7. Metzger, S. H., Jr., "Dialkyl Alkylphosphonates," U.S. 3,067,231 (December 4, 1962); *C.A.*, 58, 7976g (1963).
8. Smith, C. J., Jr., "Alkyl Phosphonates," U.S. 2,853,507, (September 23, 1958); *C.A.*, 53, 7989a (1959).
9. Hudson, R. F. and L. Keay, "The Hydrolysis of Phosphonate Esters," *J. Chem. Soc.*, 2463-2469 (1956).
10. Miller, H., SE Research Institute, Birmingham, AL, personal communication (telephone), (1975).
11. Bel'skii, V. E., G. Z. Motygullin and O. N. Grishina, "Kinetics of Dialkyl Methylphosphonate Hydrolysis," *Izv. Akad. Nauk SSR, ser. Khim.*, (12), 2813-2814 (1969); *C.A.*, 72, 78155k (1970).
12. Davis, G. T., F. Block, M. M. Demek, J. Gorrell and H. Z. Sommer, "GB Demilitarization Spray-Drying Studies," Internal Reports, Chemical Laboratory, Edgewood Arsenal, Aberdeen Proving Ground, MD (1974).
13. Bailin, L. J., M. E. Sibert, L. A. Jonas and A. T. Bell, "Microwave Decomposition of Toxic Vapor Simulants," *Environ. Sci. Technol.*, 9, 254-258 (1975).
14. Labes, M. M., C. Owens, N. M. Karayannis and L. L. Pytlewski, "Infrared and Proton Nuclear Magnetic Resonance Studies of Adducts of Tin(II) and -(IV) and Titanium(IV) Halides With Diisopropyl Methylphosphonate," *J. Phys. Chem.*, 75, 637-641 (1971); *C.A.*, 74, 105050x (1971).

15. Karayannis, N. M., C. Owens, L. L. Pytlewski and M. M. Labes, "Complexes of Diisopropyl Methylphosphonate with Metal Salts Containing Complexing Anionic Groups," *J. Inorg. Nucl. Chem.*, 32, 83-90 (1970).
16. Karayannis, N. M., C. Owens, L. L. Pytlewski and M. M. Labes, "Diisopropyl Methylphosphonate Complexes of Metal Perchlorates," *J. Inorg. Nucl. Chem.*, 31, 2059-2071 (1969); *C.A.*, 71, 66814r (1969).
17. McPhail, M. K. and P. A. Adie, "The Distribution of Radioactive Phosphorus in the Blood and Tissues of Rabbits Treated With Tagged Isopropyl Methylphosphonofluoridate (Sarin)," *Can. J. Biochem. Physiol.*, 38, 945-951 (1960).
18. Meyrick, C. I. and H. W. Thompson, "Vibrational Spectra of Alkyl Esters of Phosphorus Oxy-acids," *J. Chem. Soc.*, 225-229 (1950).
19. Moores, V. T., "Identification and Estimation of War Gases By Infra-Red Spectrophotometry," Porton Technical Paper No. 358, p. 5, (1960).
20. Lorquet, J. C. and S. Vassart, "Sarin and Its Degradation Products By Infrared Spectrography," *Bull. Soc. Chim. Belg.*, 68, 336-343 (1959).
21. Donner, R. and K. Lohs, "Cobalt Chloride in the Detection of Organic Phosphorus Ester By Paper and Particularly Thin-Layer Chromatography," *J. Chromatogr.*, 17, 349-354 (1965).
22. Plummer, J. B., "Laboratory Analysis," Report of Analysis From Shell Chemical Company, Denver, CO to Rocky Mountain Arsenal, (April 10, 1975).
23. Dunn, W. S., "Determination of DIMP (As Determined By Colorado Department of Health and Shell Chemical Company)," Chemistry Section, Laboratory Division, Colorado Department of Health, (April 10, 1975).
24. St. John, G. A. and M. Anbar, "Determination of Subpicogram Amounts of Chemical Agents In the Atmosphere," EC-CR-74028, Stanford Research Institute, Menlo Park, CA. (1974); AD/A-000 886.
25. Mavel, G. and G. Martin, "Nuclear Paramagnetic Resonance Study of Organo-Phosphorus Compounds. Seven Normal and Isopropyl Theoretical Spectral Groups of the A (A') BX Type," *J. Phys. Radium*, 24, 108-112 (1963).
26. Anonymous, "Chemical Corps Quarterly Technical Progress Report," Research and Engineering Division, Washington, DC, (July 1, 1948).

27. Ford-Moore, A. H. and B. J. Perry, "The Chemistry of the Alkane-fluorophosphonates: Part VI. The Dialkanepyrophosphonates," Porton Technical Paper No. 68, pp. 3-4, (June 29, 1948).
28. Jacobson, K. H., "The Acute Toxicity of Some Intermediates In GB Manufacture," Report No. 17, Chemical Corp Medical Laboratories, Army Chemical Center, MD, (February, 1953).
29. Wiles, J. S., Edgewood Arsenal, Aberdeen Proving Ground, MD, personal communication (telephone), Subject: "Toxicity of DIMP to Rats," (August 5, 1975).
30. Boyer, L., Vegetation Control Division, Fort Detrick, MD, personal communication (oral), (April 24, 1975).
31. Donally, G., Director of Facilities at Rocky Mountain Arsenal, personal communication (telephone), (February 21, 1975).
32. Frank, J. R., L. J. Sherman and R. A. Creager, "Defoliation Studies: II. Screening of Defoliants, Herbicides, and Desiccants," Technical Report 87, Crops Division, Biomedical Sciences Laboratory, Department of the Army, Fort Detrick, MD, (June 1967); AD 818 425.

DICYCLOPENTADIENE

ALTERNATIVE NAMES

Dicyclopentadiene; Bicyclopentadiene; Biscyclopentadiene; 3a,4,7,7a-Tetrahydro-4,7-methanoindene

PHYSICAL AND CHEMICAL PROPERTIES

CAS Reg. No. 0077-73-6

Toxic Substances List: PC 10500

Molecular formula: $C_{10}H_{12}$

Dicyclopentadiene (DCPD) is a waxy solid at room temperature with a strong camphor-like odor. The structures of DCPD appear in Figure J-1. The isomers may be considered as cis- and trans- in terms of the 2- and 8- carbons. Trans-DCPD is the usual form, (and where DCPD is cited the trans- form is understood). The cis- form has been prepared from the trans- form by a method described by Schröder (1). A 20% solution of DCPD in CS_2 was heated for 2 to 4 hours at 180° - $200^{\circ}C$ under 50 atmospheres pressure. The solvent was then distilled, and the products separated by in vacuo distillation with a 30% yield of cis-DCPD.

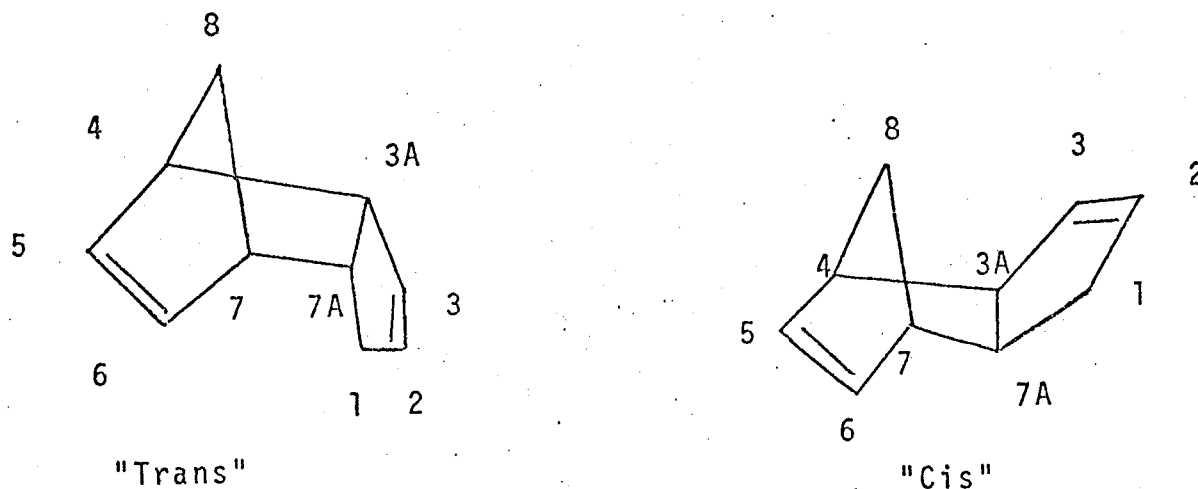


Figure J-1. Cis- and Trans- Isomers of Dicyclopentadiene

According to an article by Waring and co-workers (2), crude DCPD was distilled, and 40° - $44^{\circ}C$ range distillate (probably monomer) collected and allowed to stand overnight. The cis- isomer reportedly crystallized when the distillate was placed in vacuum, had a melting point of $27.8^{\circ}C$, and only a faint odor.

Table J-1 summarizes physical properties of trans-DCPD.

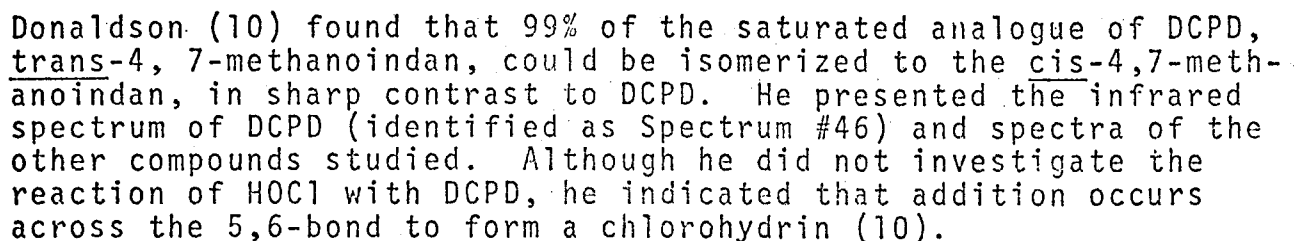
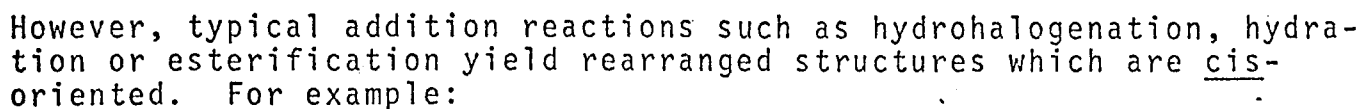
TABLE J-1

Physical properties of Trans-Dicyclopentadiene

Property	Value	References
Density at 20°C, g/cc	0.982	(3)
Melting Point, °C	32.9	(4)
n_D^{35} (Refractive Index)	1.5050	(5)
Temp, °C for cited Vapor Press, mm Hg		
20°	1.4	(3)
47.6°	10.0	(6)
105°	100.0	(3)
166.6° (boiling point)	760.0	(4)
Solubility in Water (ppm)	Considered insoluble Estimated 40*	(6) (6a)

*-Estimation on basis of solubility of diolefins of similar molecular volume (6a).

Dicyclopentadiene can be prepared by dimerizing cyclopentadiene. Harkness et al. (7) reported that the second-order rate constant for the reaction in liquid cyclopentadiene was $8.5 \times 10^5 e^{-14900/RT}$ cc/mole-sec. Thus, if one cc of cyclopentadiene is allowed to stand at 25°C for one day, 52% conversion to the dimer should occur. This result is approximate since the liquid phase changes density as dimerization proceeds. DCPD in turn can break down to the monomer. These authors (7) determined the breakdown to be a first-order reaction in the vapor phase with rate constant $10^{13} e^{-33,700/RT} \text{ sec}^{-1}$. In 1936, Khambata and Wassermann (8) reported the liquid phase rate constant as $3 \times 10^{13} e^{-35400/RT} \text{ sec}^{-1}$. At 30°C, the half-lives of DCPD breakdown in the vapor and liquid phases are calculated at 4,315 and 24,200 years, respectively. This means that the equilibrium between the monomer and dimer of cyclopentadiene lies strongly on the side of the dimer at ambient temperatures. The 584A photoelectron spectrum of DCPD was measured by Baker et al. (9). DCPD undergoes reactions involving its double bonds; some of these were studied in a thesis by Donaldson in 1958 (10). If addition is made across one double bond, it is inevitably the 5,6-bond. DCPD can be hydrogenated in the presence of Raney nickel to



Until recently, analysis for DCPD as a trace pollutant was not well developed. According to a 1967 article by Szewczyk (11), DCPD absorbs in the infrared at 677 and 1344 cm^{-1} sufficiently distinct from the cyclopentadiene peaks of 644 and 1369 cm^{-1} to permit analysis of DCPD in the presence of cyclopentadiene. Raman spectrum frequencies are found at 1571 and 1613 cm^{-1} (12). Miskalis (13) used gas chromatograph to detect DCPD in coke-oven gas. Gas chromatography of mixtures containing DCPD was reported as early as 1958 (14). Kinkead, et al. (3) used flame ionization gas chromatographic analysis (at 135°C, with a 10 ft column of 15% Tergitol NP-44 on Gas Chrom Q) to measure DCPD concentrations as low as 1 ppm in air. In work done for the Colorado State Department of Health, headspace analysis by gas chromatography was performed on water containing DCPD (15). Details of the analysis are not available, though it is claimed to detect DCPD at 0.28 ppb in water (16). DCPD in a benzene-acetic acid mixture gives a color test with bromine at a sensitivity of about 60 ppm (17). DCPD exhibits a fluorescence that might be useful for analysis (18).

24

limited toxicity data available and extrapolation from similar chemicals." Kinkead et al. (3) have suggested a hygienic standard for man of 5 ppm. The TLV for DCPD recommended by Russian workers (24, 25), is 0.185 ppm (1 mg/m³). Russian workers (26) have also recommended a permissible concentration of 0.0001 mg/l for DCPD in water supply systems. Man can detect 0.003 ppm DCPD vapor by odor (3).

The carcinogenicity of DCPD by intramuscular injection in the rat was investigated under an NCI contract at the Institute of Chemical Biology, San Francisco University (Dr. A. Furst, 1975) (27). The compound was not considered to be carcinogenic under the conditions of the experiment.

The toxicology of DCPD, including phytotoxicity, has been summarized in a fact sheet (28). The pathological effects in rats were typical of irritating hydrocarbons when administered orally in large doses; it is slightly to moderately toxic by the dermal route; and highly toxic by the oral and intraperitoneal routes in single dose studies. The lack of complete data indicates the need for further studies for an accurate evaluation of the toxic potential of DCPD. Recommendations for further toxicological studies have been made (28), and the implementation of these recommendations has already been undertaken through a USAMRDC contract with Litton Bionetics, Inc., Falls Church, Virginia 22046.

ENVIRONMENTAL CONSIDERATIONS

No information is available as to DCPD behavior in soil and water, its effects on animals in the environment, or its transmission through food chains. A USAMRDC contract study to determine the toxicity of DCPD to aquatic vertebrates and invertebrates has been initiated through Bionomics, E. G. & G., Inc., Wareham, MA 02571.

PLANTS

Tests conducted at Ft. Detrick during 1974-1975, in which wheat (Wichita) and beans (Black Valentine) were treated with diisopropyl methylphosphonate (DIMP) and DCPD combined (water solution to soil), showed a greater effect on test plants than treatments with DIMP alone. Thus an additive, or possible synergistic, effect due to DCPD was suggested. Tests conducted with DCPD alone at 10 and 40 ppm caused tip burning of leaves (29). A USAMRDC contract study to determine plant uptake and effects and soil retention of DCPD has been initiated through Aerojet Ordnance and Manufacturing Co., Downey, CA 90241.

EXISTING STANDARDS

No information available.

MAMMALIAN TOXICOLOGY

There is no published information on the toxicity of DCPD to humans. Information on the mammalian toxicity of DCPD is summarized in Tables J-2 and J-3.

TABLE J-2

Summary of Acute Toxicity of DCPD

Animal Species	Route of Administration	LD50 (mg/kg)	Range Value	References
Rat	Oral	353	262-478	3
		410	310-530	19
Rat (male)	Oral	435	361-523	20
Rat (female)	Oral	396	343-458	20
Rat	Intraperitoneal	200		21
		310		3
Mouse	Intraperitoneal	200		21
Rabbit	Dermal	5080*	3110-8290	3
		4460*	2440-8150	19
		6720*	3150-14300	22

* - LC50 values.

TABLE J-3
Inhalation Toxicity of DCPD

Animal Species	Dose (ppm) & Exposure (hr)	LC50 (ppm)	Remarks	References
Rat	4	660	Range 553-817	3
Rat		359		3
Rat		385		3
Rat	Saturated vapor	1*		3
Mouse (male)	4	145		3
Rabbit (male)	4	771		3
Rat	2500/1		1/4 killed	23
Rat	2000/4		4/6 killed	23
Rat	1000/4		4/4 killed	23
Rat	500/4		1/6 killed	23
Rat	250/6 x 10		1/4 killed	23
Rat	100/6 x 15		4/4 killed	23

* - LT 50 (hr.)

LITERATURE CITED

1. Schröder, W., "An Isomeric Dicyclopentadiene," *Angew. Chem.*, 72, 865-866 (1960); *C.A.*, 55, 9302i (1961).
2. Waring, C. E., E. E. Kern and W. A. Blann, "Dicyclopentadiene: Preparation from the Monomer; Dielectric Constants of Dimer at Several Temperatures," *J. Am. Chem. Soc.*, 63, 1767 (1941).
3. Kinkead, E. R., U. C. Pozzani, D. L. Geary and C. P. Carpenter, "The Mammalian Toxicity of Dicyclopentadiene," *Toxicol. Appl. Pharmacol.*, 20, 552-561 (1971).
4. Ottinger, R. S., J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy and C. C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste. Volume X. Organic Compounds," EPA-670/2-73-053-j, (1973).
5. Nikitina, A. N. and V. M. Safonova, "Change of Index of Refraction of Organic Liquids in a Broad Temperature Interval," *Zhur. Fiz. Khim.*, 29, 356-358 (1955); *C.A.*, 50, 13543c (1956).
6. Patty, F. A., "Industrial Hygiene and Toxicology. 2nd Revised Edition. II. Toxicology," pp. 1208-1209, pp. 1216-1217, p. 2327 (1963).
- 6a. McAuliffe, C., "Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cycloolefin, and Aromatic Hydrocarbons," *J. Phys. Chem.*, 70, 1267-1275 (1966).
7. Harkness, J. B., G. B. Kistiakowsky and W. H. Mears, "Studies in Gaseous Polymerizations," *J. Chem. Phys.*, 5, 682-694 (1937).
8. Khambata, B. S. and A. Wassermann, "Kinetics of an Inverse Diene Synthesis in the Pure Liquid State," *Nature*, 138, 368-369 (1936).
9. Baker, A. D., D. Betteridge, N. R. Kemp and R. E. Kirby, "Application of Photoelectron Spectrometry to Pesticide Analysis. Photoelectron Spectra of Five-Membered Heterocycles and Related Molecules," *Anal. Chem.*, 42, 1064-1073 (1970).
10. Donaldson, M. M., "The Chemistry of Dicyclopentadiene and Some of Its Derivatives," Doctorate Thesis, Princeton University (1958); Microfilm No. 61-1984; University Microfilms, Inc., Ann Arbor, MI, (1960).
11. Szewczyk, H., "Infrared Spectrophotometric Determination of Cyclopentadiene and Dicyclopentadiene in their Mixtures," *Chem. Anal. (Warsaw)*, 12, 709-713 (1967).
12. Treshchova, E. G., V. M. Tatevskii, V. R. Skvarchenko and R. Y. Levina, "Raman Spectra of Hydrocarbons of Different Classes. V. Raman Spectra of Some Bi- and Tricyclic Diene Hydrocarbons," *Optika i Spektroskopiya*, 5, 553-560 (1958); *C.A.*, 53, 2789f (1959).

13. Miskalis, A. J., "Gas-Chromatographic Analysis of Coke Oven Benzene-Toluene-Xylene (BTX), and Benzene for Minor Components," *Am. Chem. Soc., Div. Gas Fuel Chem., Preprints*, pp. 52-62 (1960); C.A., 57, 6224h (1962).
14. Dahmen, E. A. M. F. and J. D. van der Laarse, "Analysis of Cyclopentadiene-Containing Products With Special Reference to Gas Chromatography," *Z. Anal. Chem.*, 164, 37-48 (1958).
15. Small, M. J., "Rough Notes on Visit to Colorado State Department of Health," (8-9 April 1975).
16. Shukle, R. J., "1974-75 Groundwater Study of the Rocky Mountain Arsenal and Some Surrounding Area," Colorado Department of Health, Water Quality Control Division, (1975).
17. Palfray, L., S. Sabetay and B. Kadrinoff, "A Color Test for Dicyclopentadiene," *Ann. chim. anal. chim. appl.*, 23, 207-209 (1941).
18. Pearce, J. A. and W. A. Bryce, "Fluorescence Spectra of Extracts of Dried Whole Egg Powder," *Food Technol.*, 1, 310-319 (1947).
19. Smyth, H. F., Jr., C. P. Carpenter, C. S. Weil, U. C. Pozzani and J. A. Striegel, "Range-Finding Toxicity Data: List VI," *Am. Ind. Hyg. Assoc. J.*, 23, 95-97 (1962).
20. Calo, C. J., "Letter to Advisory Center on Toxicology, National Research Council, From the Velsicol Chemical Corporation," (October 29, 1975).
21. Christensen, H. E., T. T. Luginbyhl and B. S. Carroll (eds.), "The Toxic Substances List-1974 Edition," p. 267, p. 480, U.S. Department of Health Education and Welfare, Public Health Service Center for Disease Control, National Institute for Occupational Safety and Health, Rockville, MD, (1974).
22. Smyth, H. F., Jr., C. P. Carpenter, C. S. Weil and U. C. Pozzani, "Range-Finding Toxicity Data. List V," *Arch. Indust. Hyg. Occup. Med.*, 10, 61-68 (1954).
23. Gage, J. C., "The Subacute Inhalation Toxicity of 109 Industrial Chemicals," *Brit. J. Industr. Med.*, 27, 1-18 (1970).
24. Korbakova, A. I., "Some Urgent Problems Relating to Standard Levels of New Industrial Chemicals in the Air of Work Premises," *Vestn. Akad. Med. Nauk SSSR*, 19, 17-23 (1964).
25. Shashkina, L. F., "The Maximum Permissible Concentration of Cyclopentadiene and Dicyclopentadiene, in the Atmosphere of Industrial Premises," *Gigiena Truda i Prof. Zabolevaniya*, 9, 13-19 (1965); C.A., 64, 20509c (1966).
26. Taradin, Y. I., G. V. Buravlev, G. S. Bokareva, N. Y. Kuchmina and L. N. Shavrikova, "Toxicological Characteristics of Dicyclopentadiene," *Toksikol. Gig. Prod. Neftekhim. Neftekhim. Proizvod.*, 197-206 (1972); C.A., 81, 10203e (1974).

27. Furst, A., Letter to J. C. Dacre, (May 23, 1975).
28. Dacre, J. C., USAMBRDL, "Fact Sheet-DCPD Toxicity," (May, 1975).
29. Boyer, L., personal communication (oral), (April 24, 1975).

POWDERED CARBON COST ANALYSIS

Annual Operating and Maintenance Costs for the Interim Treatment/Containment System at RMA.

Operational Assumptions: Interim system will work at capacity (10,000 gal/hr) for 24 hours/day (3 shifts), 7 days a week, 330 days/year. The present carbon dosage of 252 mg of carbon per liter of treated water will remain at this level in the future. The same applies for the present anionic and cationic polymer dosages, .13 and 1.59 mg/l respectively. It is assumed that one full time supervisor and one operator per shift will be needed to operate the treatment unit. Once the containment system is operational, only periodic inspection will be needed.

Maintenance Assumptions: Due to the limited length of time the treatment unit is to operate, possibly up to six years, it is speculated that only routine repair and maintenance will be required. However, this statement is complicated by the fact that this unit has been inoperative for an extended period of time. Therefore, a moderate cost will be assumed.

Other Assumptions: It has been assumed that the laboratory at RMA will continue to be in direct support of the Installation Restoration Program. The quality control costs can therefore be considered part of overhead and have been included in the manpower costs.

COST CALCULATIONS

Raw Materials

Total Yearly Capacity:

$$10,000 \text{ gal/hr} \times 24 \text{ hrs/day} \times 330 \text{ days/year} = 7.92 \times 10^7 \text{ gal} = 79,200,000 \text{ gal.}$$

Carbon Costs (1)*:

At 24 cents per pound (truck load quantity),

$$(7.92 \times 10^7 \text{ gal})(252 \text{ mg/l})(3.78 \text{ l/gal})(1 \text{ gms/1000 mg})(1 \text{ # /454 gms})$$
$$(\$.24/\text{#}) = \$39,900$$

Polymer Costs (1):

At \$1.50 per pound for either coagulant,

* - Number in parenthesis refers to a corresponding reference

Cationic

$(7.92 \times 10^7 \text{ gal})(1.59 \text{ mg/l})(3.78 \text{ l/gal})(1 \text{ gm/1000 mg})(1 \text{ \#/454 gms})$
 $(\$1.50/\#) = \1580

Anionic

$(7.92 \times 10^7 \text{ gal})(.13 \text{ mg/l})(3.78 \text{ l/gal})(1 \text{ gm/1000 mg})(1 \text{ \#/454 gms})$
 $(\$1.50/\#) = \130

TOTAL RAW MATERIALS = \$41,600/yr

Operating Labor: Assume the treatment unit will operate 3 shifts per day for 7 days per week. This equals 21 shifts/week. Each operator can handle 5 shifts/week, therefore, there is a need of 5 men. This total amount of manpower covers sickness, leave, etc. All overhead costs such as administrative expenses and arsenal costs are included in the manpower rates.

At a rate of \$20 per hour for a technician at RMA (1), the operating labor cost equals; (this cost may be under estimated)

$5 (\$20/\text{hr} \times 40 \text{ hrs/week} \times 52 \text{ weeks/yr}) = \$208,000/\text{yr}$

Operating Supervision:

At a rate of \$28 per hour for an engineer (1), the operating supervision cost equals;

$\$28/\text{hr} \times 40 \text{ hrs/week} \times 52 \text{ weeks/yr} = \$58,240$

TOTAL MANPOWER = \$266,240/yr

Power & Utilities: For the treatment/containment system at RMA, no steam, fuel, refrigeration or municipally treated water is required for operation. Of the electricity to be used, the majority will go for the containment aspect. Pumping of groundwater to and from the treatment unit, intermediate pumping at theerator and the necessity of mixing, heating and lighting make-up the electrical requirements.

Only an estimate can be made of the containment utility costs due to the fact the pump tests have not been completed. WES (2) puts this estimate at approximately \$1,000 per month or \$12,000 per year.

Utility costs for the treatment unit have been estimated at 20% of the containment power costs. An alternate technique (9) is that of estimating utilities at 3% of the overall equipment costs. For the sake of comparison, both techniques have been used.

a. 20% of \$12,000/year = \$2400